

A NEW PROCESS AND EQUIPMENT FOR WASTE MINIMIZATION: CONVERSION OF NO_x SCRUBBER LIQUOR TO FERTILIZER

by

Clyde F. Parrish, Ronald G. Barile, and Paul H. Gamble
I-NET Space Services, INI-15
Kennedy Space Center, FL, 32899

Dale E. Lueck and Rebecca C. Young
NASA, DL-ICD-A and IM-ENV
Kennedy Space Center, FL 32899

ABSTRACT

A new emissions control system for the oxidizer scrubbers that eliminates the current oxidizer liquor waste and lowers the NO_x emissions is described. Since fueling and deservicing spacecraft constitute the primary operations in which environmental emissions occur, this will eliminate the second largest waste stream at KSC. This effort is in accord with the Executive Order No. 12856 (Federal Compliance with Right-to-Know Laws and Pollution Prevention Requirements, dated August 6, 1993) and Executive Order No. 12873 (Federal Acquisition, Recycling, and Waste Prevention, dated October 20, 1993). A recent study found that the efficiencies of the oxidizer scrubbers during normal operations range from 70 percent to 99 percent. The new scrubber liquor starts with 1% hydrogen peroxide at a pH of 7 and the process control system adds hydrogen peroxide and potassium hydroxide to the scrubber liquor to maintain those initial conditions. The result is the formation of a solution of potassium nitrate, which is sold as a fertilizer. This report describes the equipment and procedures used to monitor and control the conversion of the scrubber liquor to fertilizer, while reducing the scrubber emissions.

INTRODUCTION

Hypergolic propellants are used in spacecraft such as Space Shuttle, Titan, and others launched at Kennedy Space Center (KSC) and Cape Canaveral Air Station (CCAS). Fueling and deservicing spacecraft constitute the bulk of operations in which environmental emissions occur. Monomethylhydrazine (MMH), nitrogen tetroxide (N₂O₄ or NTO), and hydrazine (N₂H₄ or HZ) are the main propellants of concern. The scrubber liquor waste generated by the oxidizer scrubbers (approximately 250,000 lb/yr) is the second largest waste stream at KSC. Currently, the waste disposal cost for the oxidizer scrubber liquor is approximately \$0.20/lb or \$50,000 per year. In addition, a recent study ⁽¹⁾ found that the efficiencies of the oxidizer scrubbers during normal operations range from 70 percent to 87 percent at the Orbiter Processing Facility (OPF), and 99 percent at Launch Pads 39A and B. An emission estimate of nitrogen tetroxide at KSC based on this study ⁽¹⁾ is in excess of 200 kilograms per year. Executive Order No. 12856 (Federal Compliance with Right-to-Know Laws and Pollution Prevention Requirements, dated August 6, 1993) and Executive Order No. 12873 (Federal Acquisition, Recycling, and Waste Prevention, dated October 20, 1993) directed KSC to address the oxidizer emissions and waste disposal problems. In an effort to meet these requirements, a study was initiated to examine methods to eliminate the oxidizer scrubber liquor as a waste stream and to lower the scrubber emissions. This report covers the first phase of this study, which includes the laboratory and initial field tests.

single column of a multiple column flue gas system, hydrogen peroxide showed significant improvement in the NO_x removal^(7,8). Sodium or potassium hydroxide (KOH) with hydrogen peroxide has been used to improved scrubber efficiency for flue gases⁽⁹⁾ and for general NO_x removal from gas streams⁽¹⁰⁻¹³⁾. For example, the efficiency for NO and NO₂ removal improved from 3.8 to 46%, respectively, using 1 M KOH to 91 and 98%, respectively, when 0.12 M H₂O₂ was added to the 1 M KOH⁽¹⁰⁾. Addition of 50 ppm Cu⁺² (or Fe⁺²) improved the efficiency of a 5% NaOH/3% H₂O₂ solution from 80.6 to 93.5⁽¹¹⁾.

Currently, the KSC oxidizer scrubbers react nitrogen tetroxide and/or nitrogen dioxide with nominally 25-wt.% sodium hydroxide, which produces sodium nitrate, sodium nitrite, and nitric oxide. The spent caustic scrubber liquor could be used as a fertilizer once the pH is adjusted; however, substitution of potassium hydroxide for sodium hydroxide increases the commercial value of the scrubber liquor as a fertilizer.

The NO_x emissions from the oxidizer scrubbers have been the subject of several investigations at KSC⁽¹⁴⁻¹⁷⁾. These investigations have examined the packing materials, scrubber liquor, operating conditions, and addition of various gases in an effort to improve the performance of the oxidizer scrubbers. In one study,⁽¹⁴⁾ a falling film evaporator, used to generate a constant flow rate of NO₂ to the scrubber, produced inlet concentrations from 3,200 to over 200,000 parts per million (ppm). The flow rates of gaseous nitrogen (GN2) vented through the scrubber ranged from 0 to 700 standard cubic feet per minute (scfm). As the GN2 flow rate increased, the efficiency decreased; for example, at 150 scfm the efficiency was approximately 90 percent and at 300 scfm the efficiency fell to 60 percent. In addition, when oxygen was added to the GN2, the efficiency of removal of NO increased.

A second series of tests at KSC⁽¹⁵⁾ used "Flexiring" and "Sulzer" packing (manufactured by Koch Engineering Company) instead of ceramic saddles, and showed little change in the efficiency of the scrubbers. One interesting observation was the decrease in the efficiency as the inlet concentration decreased for the same GN2 flow rate; for example, at 50 scfm with an inlet concentration of 60,000 ppm, the efficiency was 98 percent and, with an inlet concentration of 500 ppm, the efficiency was 60 percent.

A change of the scrubber liquor from 25-weight-percent sodium hydroxide to 11.6-weight-percent sodium sulfite and 5-weight-percent sodium hydroxide in towers 3 and 4 of the scrubbers was recommended because of the increased efficiency^(16,17). For example, at 400 scfm and 8,400 ppm inlet concentration, the efficiency for 25-weight-percent sodium hydroxide was 55 percent but with 11.6-weight-percent sodium sulfite and 5-weight-percent sodium hydroxide, the efficiency was 98 percent. However, the change from 25-weight-percent sodium hydroxide to sodium sulfite blend was not made due to safety considerations.

The addition of ozone to the GN2 stream has been examined on the laboratory scale and a significant increase in the scrubber efficiency was found⁽¹⁸⁾. For example, when the inlet concentration was 25,800 ppm, the efficiency was 95.8 percent without ozone; and when the inlet concentration was 23,100 ppm, the efficiency was 99.6 percent with ozone.

As part of a project to develop an ecologically safe method for the demilitarization of MK 24 and MK 45 aircraft parachute flares, field tests were performed on sodium nitrate extracted from the process⁽¹⁹⁻²¹⁾. These tests, conducted by Purdue University, monitored the effectiveness of this waste sodium nitrate as a fertilizer. A typical MK 24 or MK 45 parachute flare contains a mixture of 10.4 lb. of magnesium, 6 lb. of sodium nitrate, and 0.6 lb. of a binder. The pilot plant process separated the magnesium from the sodium nitrate. The sodium nitrate was in the form

INSTRUMENTATION

Figure 1 shows a diagram of the laboratory scrubbers used to lower the concentration of the oxidizer before it was released to the laboratory fume hood, and to provide a test scrubber for the development of a new scrubber liquor. The design of the laboratory scrubbers is similar to the full-scale scrubbers used at KSC.

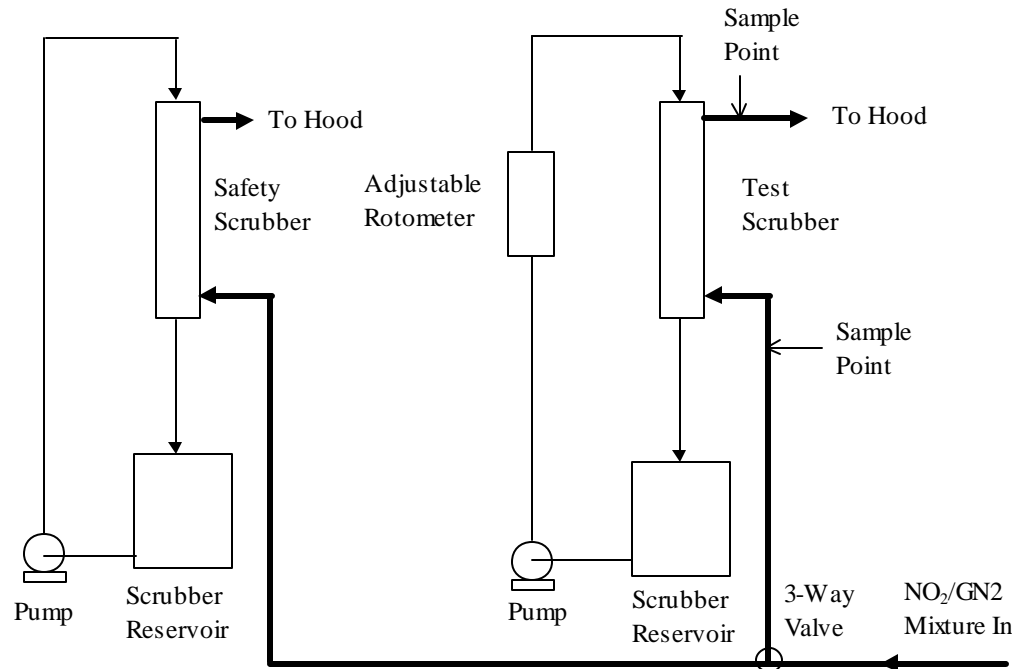


Figure 1. Laboratory Test Scrubber and Safety Scrubber

The laboratory scrubbers have glass columns 3 inches in diameter and are packed with pieces of Tri-Pac 2-inch polypropylene spheres manufactured by Tri-Mer Corporation. The safety scrubber liquor (25-percent sodium hydroxide) is pumped from a reservoir to the top of the column where it flows down to the reservoir. Gaseous nitrogen tetroxide (N_2O_4 in GN₂) flows up the column and exits to the fume hood. This configuration lowers the concentration of oxidizer, which is produced by the sample systems, to levels acceptable for the fume hood.

The test scrubber was equipped with an adjustable rotometer to control the flow rate of the scrubber liquor. Two sample points, one just before the scrubber and a second just after the scrubber, were used to measure the scrubber efficiency. A 3-way valve was used to direct the N_2O_4 /GN₂ flow to the safety scrubber during start-up. Once stable flow of the test gas was established the valve was rotated to the test scrubber. The test scrubber could be operated either in a scrubber liquor recirculating mode or in a single pass mode, where a second reservoir was used to collect the scrubber liquor from the scrubber. Both the safety scrubber and the test scrubber vent to the laboratory fume hood.

In order to maintain the hydrogen peroxide concentration in the scrubber liquor, a portion of the liquor is

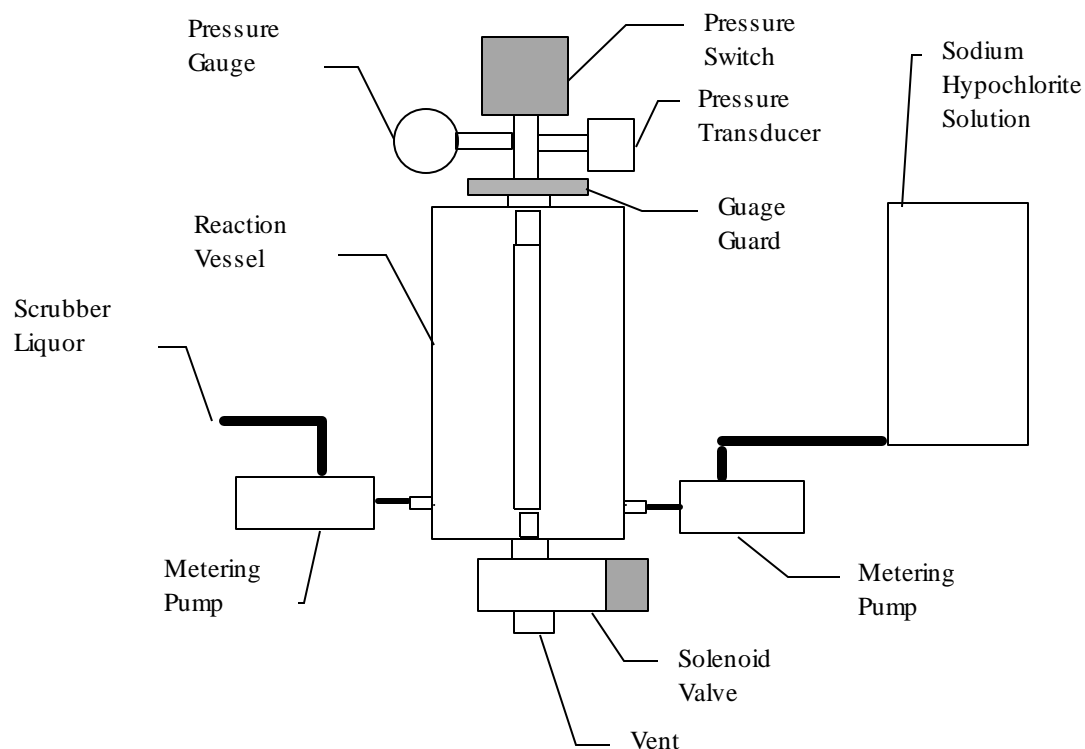


Figure 2. Hydrogen peroxide concentration control system

The reaction vessel was constructed from a 2.25-inch O.D. KYNAR rod. The volume of the reaction chamber is approximately 10 mL. The pressure switch, pressure transducer, and gauge are isolated from the reaction chamber with a gauge guard that has a Teflon diaphragm. A solenoid valve is attached to the bottom of the reaction vessel. Two metering pumps supply the scrubber liquor test solution and sodium hypochlorite solution. All wetted parts of this system are made from polymeric materials that are compatible with sodium hypochlorite and/or sodium nitrate. The electrical control system is used to maintain the concentration of hydrogen peroxide in the scrubber liquor. This system consists of a sequence timer, relay, pumps, valves and pressure switch. The sequence timer controls the addition of the reagents (scrubber liquor and sodium hypochlorite), the vent valve, and the hydrogen peroxide metering pump.

Cole-Parmer model H-56025-40 proportioning pH controller with adjustable flow rates (0 to 5.2 GPH) was selected to control the pH of the scrubber liquor for the laboratory and field tests. This controller responds to 0.1 pH unit changes and can be set to adjust the pH with acid or base feeds. The pumping rate decreases proportionally until the set point is reached. All wetted parts consist of polypropylene, PTFE, and Viton. The unit has an internal isolation transformer to protect the electronics from line voltage fluctuations. This unit is installed in the purged cart that contains the hydrogen peroxide and sampling systems.

Figure 3 is a block diagram of the sample generating system for the field validation tests, which was used in a previous project ⁽¹⁾. The storage tanks at the oxidizing farms of Beds 20A and 20B each have a CNO purge line for a

provide flows of 100, 200, 300, 400, and 500 scfm through the scrubber. This manifold configuration allows the field tests to cover the range of flow conditions found at KSC scrubbers.

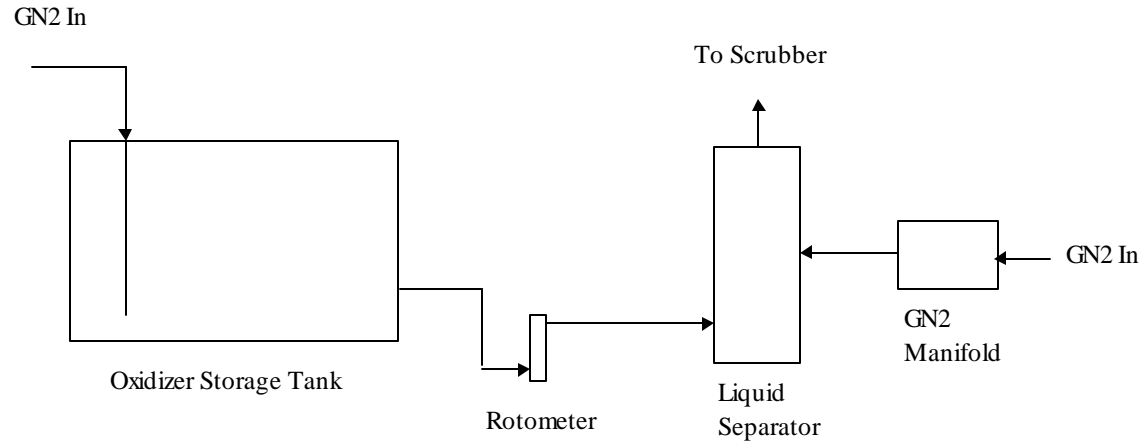


Figure 3. Diagram of the field hypergol sample generating system

The process control system (see Figure 4) used for the field validation was tested with the continuous tests in the laboratory. This system is packaged in a purged cart, which can be used in hazardous locations. The system is designed so that the scrubber liquor pump is used to circulate a small flow of sample from the pump discharge line through a line to the purged cart and back to scrubber liquor storage tank. A sample is collected from the line

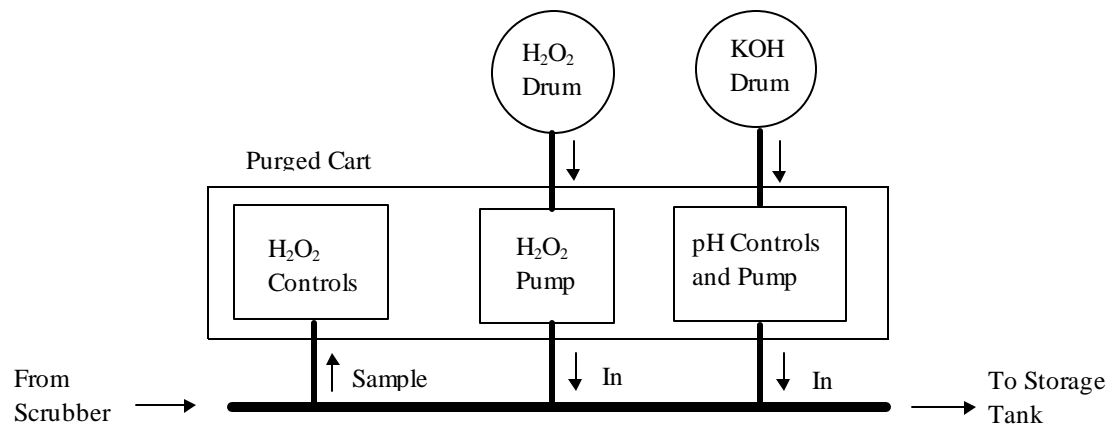


Figure 4. Block diagram of the field process control system.

at the cart for hydrogen peroxide concentration measurement and pH measurements and either/or hydrogen peroxide or potassium hydroxide are pumped into the line before it is returned to the scrubber liquor storage tank

separated from GN2(or air), and the GN2 is pulled through a rotometer to the PIAB pump; (3) sample collection system, which pumps the impinger solution that contains the sample from the liquid separator, through the pump head and then through a 3-way valve where a sample container may be filled or the sample solution pumped to waste; and (4) a purge system that can blow GN2 through the two-phase sample line from the liquid separator, through the mixing tee, where impinger solution may be added, and into the scrubber vent. This last operation allows the sample inlet system to be cleaned and dried before a sample is collected. The pumps and other electrical components are contained in the purged sample cart.

PROCEDURES

This project was divided into a laboratory proof-of-concept (POC) study and a full-scale study. The laboratory POC study measured the effects of hydrogen peroxide with and without added acid or base as the scrubber liquor, and the effects of a change from sodium hydroxide to potassium hydroxide. These studies will provide data on the scrubber efficiency, quality of fertilizer, and an estimate of the costs savings. The laboratory POC study was done at approximately 1000 ppm of NO₂ in GN2 with total gas flow rates of 3, 10, or 20 L/min and a scrubber liquor flow rate of 150 mL/min, which gave L/G ratios of 42, 12.6 or 6.3, respectively. The pH of the scrubber liquor ranged from 1.7 to 25 wt-% NaOH and the concentration of hydrogen peroxide ranged from 0.1 to 5 vol-%. The oxidizer area of KSC's hypergol storage farm for Pad 39B was used for the full-scale tests. These full-scale tests used the sampling system developed previously ⁽¹⁾ to measure the scrubber efficiencies for NO₂ concentrations of approximately 5000 ppm and flow rates from 100 to 500 SCFM. The analytical methods used for the laboratory phase of this study were used for the full-scale tests.

The analytical methods described in this section were required to analyze the used scrubber liquor, the hydrogen peroxide concentration in the test scrubber liquors before use, and the gas-phase emissions from an oxidizer scrubber for this study. Initially, the gas-phase analytical method for NO_x used ASTM method D 1608-77⁽²³⁾, which had previously been used to develop a new procedure for monitoring the emissions from the oxidizer scrubbers at KSC ⁽¹⁾. Although this method is useful over the range from 5 to 2000 ppm, the procedure is very slow and labor intensive. Therefore, a new method, based on ion chromatography, was developed. Analysis of the scrubber liquor was complicated by the presence of two oxidizing agents, nitrate ions and hydrogen peroxide, and nitrite ions, which meant that analytical methods based on oxidation/reduction characteristics of the analyte could not be used. Analysis of the scrubber liquor was important, first, to study changes that occurred due to different scrubber liquors, and second, for the development of a process control system.

Hydrogen peroxide concentrations were measured by titrating with KMnO₄ and FTIR methods. A colorimetric method was developed for assaying hydrogen peroxide in scrubber liquors, that contained nitrite and nitrate ions, and employed anion exchange resins. Standard solutions of NO_x ions and peroxide were mixed with the resins, after which nitrite was assayed by the Saltzman method and nitrate by ASTM D 1608. Both Amberlite IRA-400 and Dowex Macroporous Resin MSA-2 worked well in absorbing NO_x ions. These results indicated that nitrate and nitrite ions were removed to the extent that there was no interference to peroxide titration's with KMnO₄. Rotometers were used to measure the flow rates of the scrubber liquor.

The IC method was based on standard anion techniques and used a HP DX 500 IC system that operated under their PeakNet Chromatography Workstation software. The DX 500 system is based on a LC20 enclosure, GP40 gradient pump, ED40 electrochemical detector, and an AS40 automated sampler. An AS4 column was used for the

NO₂. Second, the laboratory scrubber was operated in a continuous mode where the scrubber liquor circulated from a reservoir to the scrubber packing and returned to the reservoir. Finally, there will be tests of a full-size scrubber (Pad 39B) to monitor changes in the scrubber efficiency and to prepare samples of scrubber liquor to be evaluated as a fertilizer. In addition to these primary objectives, methods to control the concentration of the scrubber liquor and analytical methods to measure the concentrations were developed and tested in the laboratory and field at Pad 39B oxidizer farm.

The effect of pH on the efficiency appears to pass through a maximum around a pH of 7 and then drops on either side for the single pass laboratory tests, see Figure 5. In these tests the scrubber liquor was pumped to the scrubber and to a waste container and samples were collected and tested for nitrite, nitrate, and hydrogen peroxide concentrations and pH. Typically, there was a significant drop in the pH during the single pass runs. For example, when water was used as the scrubber liquor (initial pH 7) the pH dropped to 2 for a single pass through the scrubber when the NO₂ concentration was 1000 ppm.

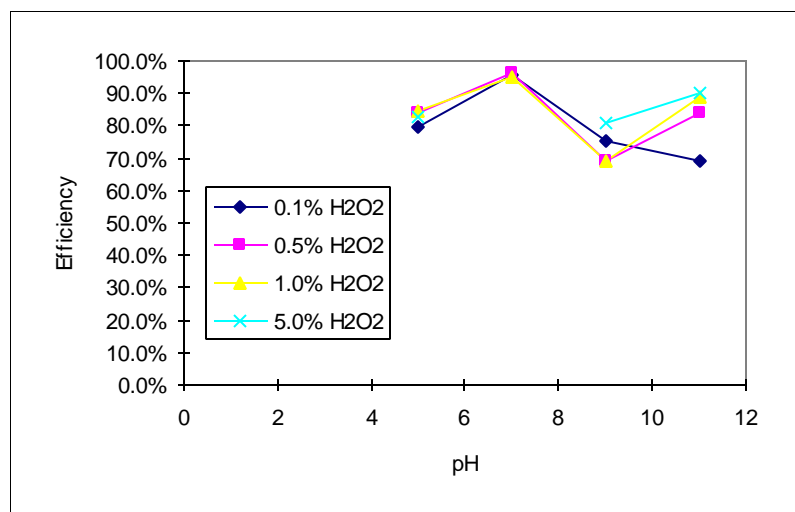


Figure 5. Efficiency vs pH at various peroxide concentrations at L/G of 12.6

The same decrease in efficiency with pH around 7 was observed in the continuous runs as well, except in this case the pH range extended beyond the range of the single pass tests and then the efficiency appeared to increase. These changes for the continuous laboratory experiments are illustrated in Figure 6. Increase in peroxide reactivity has been observed for acidic and alkaline solutions and has been attributed to the increased instability of hydrogen peroxide.

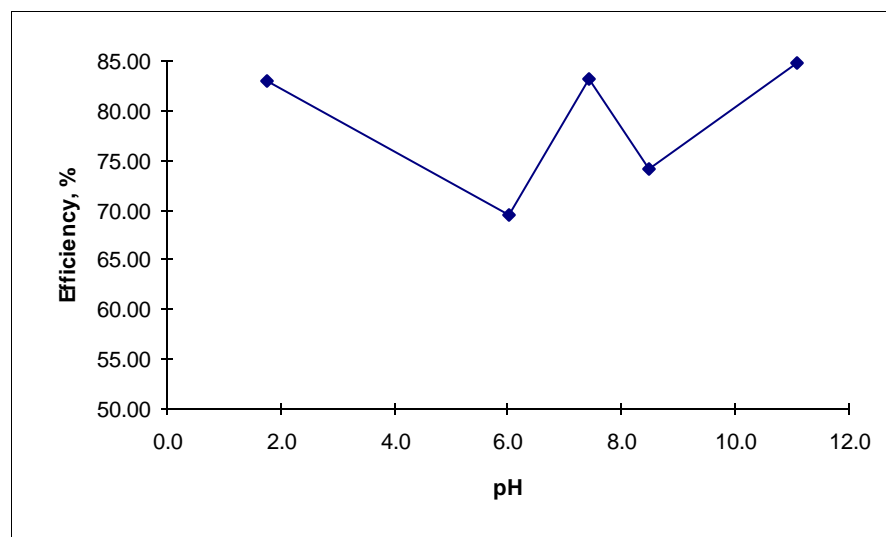
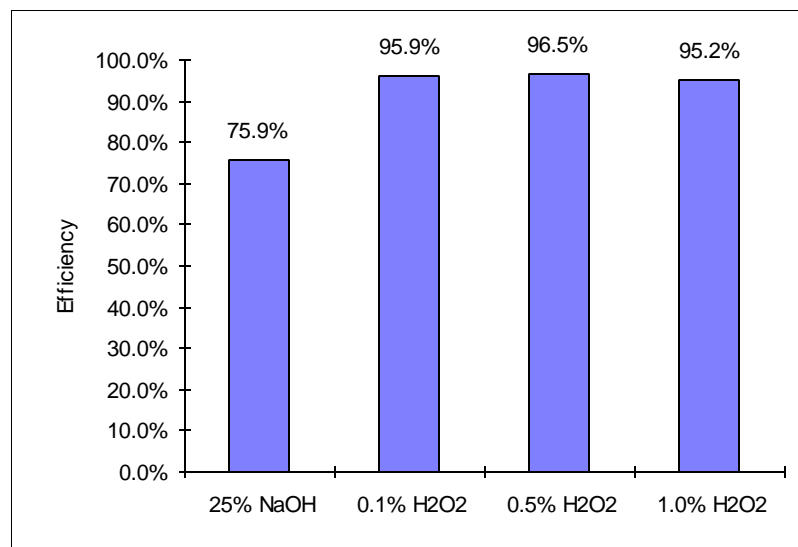


Figure 6. Efficiency vs. pH for continuous laboratory runs at 1% hydrogen peroxide and approximately 1000 ppm of NO_2

The effect of hydrogen peroxide on the efficiency is illustrated in Figures 7 and 8. These represent tests where the pH was held constant and the amount of hydrogen peroxide was varied. Figure 7 illustrates the results where the peroxide concentration is increased from 0.1 to 1.0 percent which shows efficiencies around 96% as compared to an efficiency of around 76% for 25-wt% sodium hydroxide.



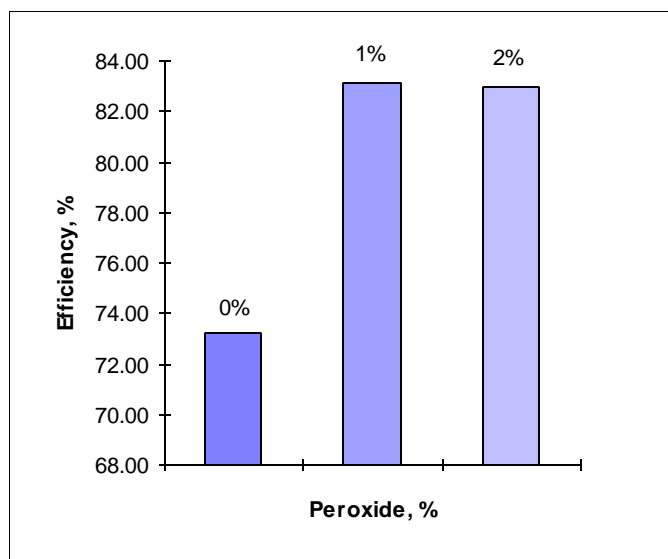


Figure 8. Effect of hydrogen peroxide on the efficiency of the laboratory scrubber for continuous runs

Analysis of the scrubber liquors for the presence of nitrite ions indicated that the oxidation with hydrogen peroxide had oxidized all of the nitrite ions to nitrate ions, which was one of the objectives for the addition of hydrogen peroxide to the scrubber. Without the presence of hydrogen peroxide the concentration of nitrite and nitrate ions is almost equal. Since nitrite ions disproportionate to form nitric oxide and nitrate ions, oxidation of the nitrite ions is desirable to lower the emissions of NO.

CONCLUSIONS

The primary objectives of this study were achieved: to develop a new scrubber liquor that was less expensive to use than the current 25-wt% sodium hydroxide when all factors were considered including waste disposal, preparation of the scrubber liquor, and handling a hazardous waste (the spent oxidizer scrubber liquor). Improvement in the scrubber efficiencies is the second most important accomplishment of this study, and these changes are significant.

A convenient method for control of the hydrogen peroxide concentration was developed for this study. This device uses the pressure generated when hydrogen peroxide is decomposed with bleach to sense the concentration of hydrogen peroxide in the scrubber liquor.

BIBLIOGRAPHY

1. Parrish, C. and R. Barile, "Hypergolic Oxidizer and Fuel Scrubber Emissions Report", KSC-DL-3332, September 30, 1994.
2. "Wet Chemical Procedure for the Removal of Oxides from Flue and Waste Gases," *WLB, Wasser, Luft Boden*, **36**(5), 53-54, 5 (1993). 0141-7322/93/010037

7. "Process for Removing Oxides of Nitrogen from Flue Gases," Ger. Patent WO 8900449, 1989, CA**111**(2):11958e.
8. "Removal of Sulfur Dioxide and Nitrogen Oxides from Flue Gases," Ger. Patent DE 3436699, 1986, CA**104**(26):229790w.
9. "The Use of Hydrogen Peroxide for the Control of Air Pollution," *Stud. Environ. Sci.*, **34**, 275-92, (1988), CA**110**(18):159688s.
10. "Gas Scrubber Using an Alkali Solution Containing Hydrogen Peroxide," Japan Patent JP 48101378, CA**80**(26):148789m.
11. "Absorbing Nitrogen Oxides from a Waste Gas with a Solution Containing Hydrogen Peroxide, Hydroxide, and Cupric or Ferrous Ions," Japan Patent JP 49008465, CA**80**(26):148804n.
12. "Nitrogen Oxide Removal from Gases by Scrubbing," Japan Patent JP 52085979, CA**88**(10):65480t.
13. "Conversion of Nitrogen Oxides to Potassium Nitrate in Waste Gas Treatment," Japan Patent JP 50033981, CA**10**(10):67485k.
14. "Hypergolic Nitrogen Tetroxide Vapor Scrubber, Phase I Test Report," KSC-DD-777, November 1983.
15. "Final Report, Hypergolic Vapor Scrubber, Phase II (N₂O₄) & Phase III (MMH) Modification and Test Project," KSCE-3084, December 1986.
16. "Sulfite-Caustic Tail Gas Scrubber System Test Report and Recommendations," KSCE-824-0010, August 1988.
17. "Hypergolic Oxidizer Vapor Scrubber Report Phase IV & Phase V Test Results," KSCE-824-0014, April 1989.
18. Parrish, C., "Final Report, KSC Launch Site Shuttle Nitrogen Tetroxide N₂O₄ Prototype Scrubber Test Requirements Document," Contract 704357, LSOC, December 1992.
19. "A 1/10 Scale Pilot Plant for the Ecological Demilitarization of MK 24 and MK 45 Aircraft Parachute Flares," NWSC/CR/RDTR-3, US NAD Crane, Crane, IN, 17 July 1972.
20. "Ecological Demilitarization of MK 24 and MK 45 Aircraft Parachute Flares," NWSC/CR/RDTR-212, US NAD Crane, Crane, IN, 27 July 1972.
21. "Ecological Demilitarization of MK 24 and MK 45 Aircraft Parachute Flares," NWSC/CR/RDTR-213, US NAD Crane, Crane, IN, 27 July 1972.
22. Private communications, The Foxboro Co, M. Frant (currently with Orion Research), 1983.
23. ASTM D 1608-77, "Standard Test Methods for Oxides of Nitrogen in Gaseous Combustion Products (Phenol-Disulfonic Acid Procedures)," American Society for Testing Materials, ASTM Committee on Standards, 1916 Race Street, Philadelphia, PA 19103-1187.